

POLYCYCLIC AROMATIC HYDROCARBONS IN ALH84001 ANALYZED WITH TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY.

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Introduction: The discovery of polycyclic aromatic hydrocarbons (PAHs) on fresh fracture surfaces of the Martian meteorite ALH84001 is interpreted as a major clue to ancient life on the planet Mars [1]. The presence of PAHs itself is no evidence for biological processes but the same fracture surfaces of ALH84001 show carbonates with internal structures resembling terrestrial microfossils. Both observations were made by using completely different analytical techniques which, simply from their spatial resolution, do not allow a correlation of their results. Due to the small size of the supposed microfossils, 100 nm in longest dimension and 20–80 nm across, a field emission scanning electron microscope (FEG-SEM) with a lateral resolution of about 2 nm had to be used [1]. PAHs were identified by microprobe two-step laser mass spectrometry ($\mu\text{L}^2\text{MS}$) with a spatial resolution of about 50 μm and a meaningful mass spectrum was obtained by mapping a surface region of $750 \times 750 \mu\text{m}^2$ [1]. Therefore, a correlation of PAHs even with carbonates, typically 50 μm in size, could not be confirmed by these techniques although the authors suggest an association [1].

In this study we report first results on the distribution of PAHs in ALH84001 obtained by time-of-flight secondary ion mass spectrometry (TOF-SIMS).

Analytical techniques: TOF-SIMS is based on the mass analysis in a time-of-flight spectrometer of positive or negative secondary ions sputtered from the uppermost monolayers during primary ion bombardment. Not only atomic ions are generated but also large molecules survive the sputtering process, at least as characteristic fragments [2, 3]. Today TOF-SIMS is primarily used for applications in material sciences, ranging, *e.g.*, from microelectronics to the study of synthetic polymers or large biomolecules [4]. In cosmochemistry TOF-SIMS has mainly been used for the analysis of lateral element distributions in meteorites, interplanetary, and interstellar dust [5–8] but also for the search of fullerenes in interplanetary dust [9].

In this study the samples were bombarded using a Ga^+ primary ion beam with 15 ns pulse length resulting in a moderate mass resolution up to $m/\Delta m=2000$ which allow to separate atomic ions from hydrocarbons. TOF-SIMS images showing the lateral ion distribution were obtained with a primary ion beam diameter of about 0.2 μm

Sample: A demountable polished thin section of ALH84001 (#205a), initially studied by scanning

electron microscopy (SEM), was used in this TOF-SIMS study. From the SEM results we selected four different areas, between 100×100 and $150 \times 150 \mu\text{m}^2$ in size. Besides orthopyroxene, the major phase in ALH84001, these areas are dominated by carbonates, feldspatic glass, and, in one area, apatite.

Prior to our analysis any carbon coating from the SEM analysis was removed. Surface contamination was reduced by sputtering with a high intensity ion beam.

Results: Besides the atomic secondary ion distribution reflecting the mineral chemistry, we observed a complex molecular TOF-SIMS spectrum for all analyzed areas. As seen before in ALH84001 [1] little alkylation was found and principle peaks appeared at 178, 202, 228, and 252 amu, indicative for PAHs like $\text{C}_{14}\text{H}_{10}$, $\text{C}_{16}\text{H}_{10}$, $\text{C}_{18}\text{H}_{12}$, and $\text{C}_{20}\text{H}_{12}$. An example mass spectrum from an area containing orthopyroxene, feldspatic glass, and apatite is given in Fig. 1. Relative maxima were found between 115 and 252 amu with mass differences of 11 or 13 amu. Different from results obtained by $\mu\text{L}^2\text{MS}$ [1] the TOF-SIMS spectra show also characteristic peaks at lower masses such as 128 and 152 amu. Positively charged radical ions were found at 115, 141, 165, 189, 215, and 239 amu. A general trend of decreasing secondary ion intensity with increasing mass was observed.

The high lateral resolution ($\sim 0.2 \mu\text{m}$) during ion imaging allowed to search for possible enrichments of PAHs within single mineral phases. The distribution of PAHs in ALH84001 seems to be rather uniform. However, compared to orthopyroxene or feldspatic glass, carbonates showed a slight depletion of PAHs and a more pronounced depletion was found in apatite.

Several efforts were made to exclude contamination effects. We found no indication for the presence of PAHs in the embedding material. Here the secondary ion intensity of characteristic PAH peaks is up to two orders of magnitude below the maximum observed in ALH84001. A section of Chassigny [10] treated like the ALH84001 sample and investigated directly before and after our analysis showed no PAHs. Therefore, a general contamination in our laboratory can be excluded. Since surface contamination is often a problem in TOF-SIMS we compared secondary ion spectra before and after sputtering. No decrease of the PAH signal but even a slight increase during sputtering was observed.

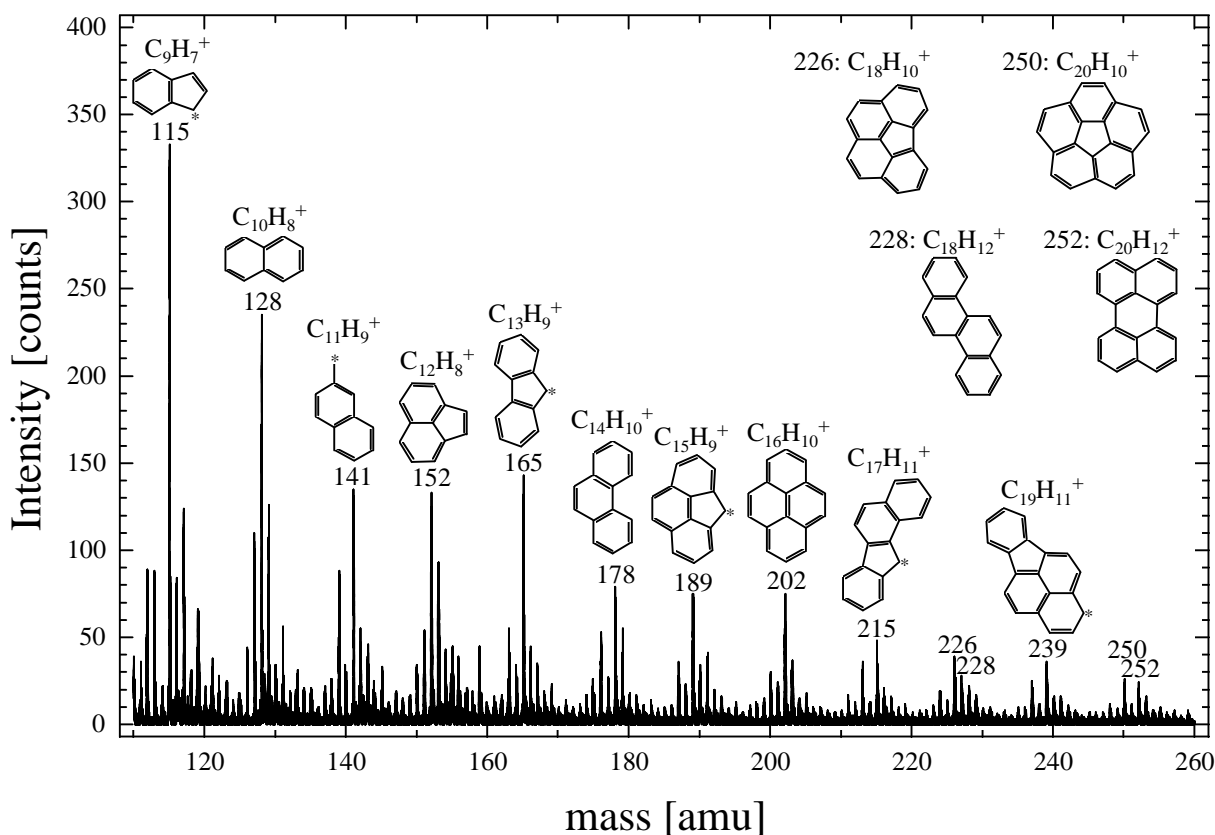


Fig. 1. Typical TOF-SIMS spectrum of mass range 110–260 amu for ALH84001. Relative maxima are separated by mass differences of 11 or 13 amu, respectively. Often both maxima appear. Relative intensities vary between different mass spectra. *E.g.*, in some spectra the peak at 228 amu dominates over the peak at 226 amu. The general trend, decreasing intensities with increasing mass, observed in all spectra, results from fragmentation during the SIMS process. Since several structural isomers exist for all mass peaks only examples for major peaks are given.

Discussion: The mass spectra from PAHs in ALH84001 obtained by TOF-SIMS (Fig. 1) differ significantly from those obtained by $\mu\text{L}^2\text{MS}$ [1]. This can be explained by differences in the ionization process. During sputtering with the primary ion beam fragmentation of the PAHs occurs and therefore the observation of low mass PAHs and especially radicals is not surprising.

A laboratory contamination theory for the PAHs can be ruled out since no PAHs were detected in our embedding material and sputtering of our sample surface did not decrease their secondary ion signal.

The origin of PAHs in ALH84001 cannot be deduced from the TOF-SIMS measurements alone. Nevertheless, there is no evidence for a correlation with carbonates – on the contrary, here they seem to be slightly depleted – or any structure within the carbonates like the supposed Martian microfossils.

Conclusion: Whether or not the structures observed in carbonates of ALH84001 represent ancient extraterrestrial life or can be explained differently [11], they have no connection with PAHs, regardless whether the

PAHs are coming from Mars or from the polar ice [12].

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